

Hydrogen Storage in Carbon Single-wall Nanotubes

*A.C. Dillon, K.E.H. Gilbert, P.A. Parilla, C. Horbacewicz, J.L. Alleman, K.M. Jones, and M.J. Heben
(Primary Contact)*

National Renewable Energy Laboratory

1617 Cole Blvd.

Golden, CO 80305

Phone: (303) 384-6641; Fax: (303) 384-6655; E-mail: michael_heben@nrel.gov

DOE Technology Development Manager: Sunita Satyapal

Phone: (202) 586-2336; Fax: (202) 586-9811; E-mail: Sunita.Satyapal@ee.doe.gov

Objectives

- Develop reproducible hydrogen capacity measurements and sample preparation methods.
- Meet the DOE hydrogen storage goals of 4.5 wt% H₂, 1.2 kWh/L by 2005.
- Optimize scalable methods for the production and purification of carbon single-wall nanotubes (SWNTs) and other nanostructured carbons for hydrogen storage.
- Gain better understanding of the hydrogen adsorption mechanisms for carbon nanotube/metal composites, particularly the importance of how, and in what form, the metal is incorporated into the SWNTs.
- Develop new methods for controlled metal incorporation in purified, cut SWNT samples.
- Probe other carbon systems for potential high hydrogen storage capacities at near ambient conditions.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- C. Durability
- D. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology

Approach

- Establish Carbon Materials Working Group (CMWG) to develop sample handling and measurement protocols and improve reproducibility of capacity measurements.
- Improve purification technique to efficiently remove graphite-encapsulated metal particles present in SWNT materials generated by a wide variety of techniques.
- Develop a low-cost, gas-phase, continuous process for carbon nanotube production employing hot wire chemical vapor deposition (HWCVD).
- Fabricate carbon nanotube samples containing iron particles of differing sizes and occurring at different but specific sites and determine the hydrogen storage properties of these highly specific samples.

- Employ TiI_4 vapor transport to deposit small Ti particles in purified, cut SWNT samples. Employ thermal evaporation of Ti to deposit thin metallic films on purified, cut SWNT samples.
- Analyze the hydrogen storage properties of conducting carbon polymers supplied by Prof. Alan MacDiarmid at the University of Pennsylvania.
- Analyze the hydrogen storage properties of HWCVD generated nano-crystalline graphite doped with iron nanoparticles.

Accomplishments

- Incorporated a CO_2 oxidation step in the purification process to remove graphite-encapsulated metals more completely.
- Developed a low-cost, scalable HWCVD technique for the continuous production of carbon multi-wall nanotubes (MWNTs) and demonstrated the potential of the same technique for SWNT production.
- Discovered that the activation of hydrogen storage on carbon nanotubes at near ambient conditions is dependent on the incorporation of small metal particles in highly intimate contact with the tube structure.
- Determined barriers to Ti incorporation via both vapor transport and evaporation, but gained significant knowledge to focus on efforts with higher likelihood of success in future investigations.
- Discovered unanticipated hydrogen storage capacities on HWCVD generated nano-crystalline graphite doped with iron nanoparticles.
- Performed preliminary assessment of the adsorption of hydrogen on conducting polymer samples provided by Prof. Alan MacDiarmid of the University of Pennsylvania.

Future Directions

- Establish, contingent upon DOE's approval, a DOE-sponsored Virtual Center of Excellence for the study and advancement of carbon-based hydrogen storage materials. The Center plans to bring together experts from national labs, universities and industry, including Nobel Laureate, Prof. Richard Smalley of Rice University, and Dr. Guido Pez of Air Products and Chemicals, Inc.
- Gain a better understanding of the mechanistic processes associated with hydrogen binding on nanostructured carbon materials.
- Develop reproducible methods to activate materials to high, room-temperature capacities (>4 wt%).
- Utilize computational chemistry to provide a link to and guidance for experimental efforts.
- Establish high-throughput experimental methods to rapidly evaluate nanostructured carbon hydrogen storage materials.
- Use knowledge obtained from this year's research to establish a better method for the controlled incorporation of metal into nanostructured carbon materials.
- Continue exploring alternative nanostructured carbon materials for room-temperature hydrogen storage, including aromatic cage compounds containing transition-metal ions.

Introduction

The decreasing fossil fuel supply and the growing number of densely populated metropolitan cities with poor local air quality have spurred an initiative to develop an alternative to petroleum motor fuels. Hydrogen, which may be produced

from renewable sources, has emerged as one of the most promising candidates for the replacement of the current carbon-based energy services. Although hydrogen could supply all of the world's vehicular energy demands¹, a major impediment to the implementation of this new fuel is the lack of a convenient, cost-effective on-board storage system.

Compact, lightweight carbon adsorbent materials have become potential candidates for use in a hydrogen storage system. Of particular interest are the “engineered” nanostructured carbons such as carbon single-wall and multi-wall nanotubes (SWNTs and MWNTs) and graphitic nanoparticles or cages. Interestingly, the presence of small quantities of transition metals has been shown to enhance the hydrogen adsorption capacities of graphitic materials². The long-term goal of the project is to enable efficient adsorption of hydrogen at ambient temperature and pressure on nanostructured carbon materials at system energy densities specified by DOE (4.5 wt% H₂, 1.2 kWh/L by 2005).

Approach

Laser-vaporization³ and a simple purification technique⁴ have been employed to generate SWNTs for hydrogen storage applications. However, the current purification process is not effective for the removal of graphite-encapsulated metals. Also, the laser process is not scalable for industrial production of carbon nanotubes. A CO₂ oxidation step has been added to the purification process in order to aid in the removal of graphite-encapsulated metals. Also, a continuous and potentially scaleable HWCVD technique has been developed for the production of carbon nanotubes.

Building on past research, which has shown that transition metal catalysts lead to enhanced hydrogen storage capacities on graphitic nanostructured materials², experiments were performed to understand the nature of the metal/carbon interaction as well as to control the incorporation of metal into cut, purified carbon SWNT samples. Finally, hydrogen storage properties of non-nanotube carbon materials were explored in detail.

Results

Improvements in SWNT Purification and Development of HWCVD Process for Continuous Carbon Nanotube Production. Graphite-encapsulated metals are not removed via our current purification process (16-hr reflux in 3 M HNO₃ followed by air oxidation at 550°C)⁴. By employing oxidation in CO₂ prior to the dilute acid reflux, a

reduction in the analysis metal content in the final purified materials is observed. Figure 1 shows thermal gravimetric analysis (TGA) curves for air oxidation of a SWNT material following the 3 M HNO₃ reflux and the same material subjected to CO₂ oxidation prior to the acid reflux. The weight of the material remaining in both TGA curves corresponds to the presence of a metal oxide residue. The metal oxide residue has been reduced by approximately a factor of two in the material that was oxidized in CO₂ prior to the acid reflux. Apparently, this oxidation cracks the graphite-encapsulation, allowing for better digestion of the metal during the acid reflux.

If nanostructured carbons are to be employed in vehicular hydrogen storage applications, continuous and scalable production techniques must be developed⁵. Hot wire chemical vapor deposition (HWCVD) has been adapted to be a continuous growth process for high-density carbon multi-wall nanotubes (MWNTs). MWNT growth is optimized in 1:5 CH₄:Ar at 150 Torr with reactor temperatures of 400 and 550°C for static and flowing gases, respectively. Ferrocene is employed to provide a gas-phase catalyst. Highly graphitic nanotubes can be continuously deposited with iron content as low as 15 wt.% and carbon impurities below TGA detection

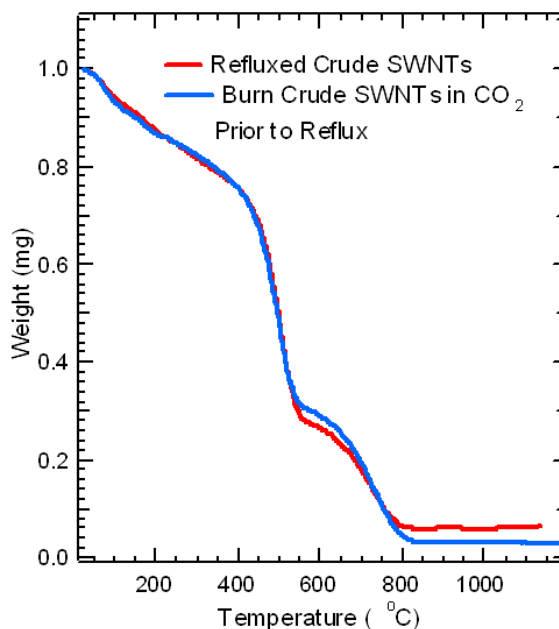


Figure 1. TGA Spectra for Air Oxidation of an SWNT Material Following the 3 M HNO₃ Reflux and the Same Material Subjected to CO₂ Oxidation Prior to the Acid Reflux

limits. The MWNTs are simply purified to >99.5 wt.% with minimal structural damage and with a 75 wt.% yield⁶. Figure 2 (top) shows a matt of high purity MWNTs produced by this technique. The production of isolated SWNTs⁷ and small bundles of SWNTs have also been achieved with a similar HWCVD technique without employing an external furnace to increase the reactor temperature. Figure 2 (bottom) shows isolated SWNTs produced by the HWCVD method. Increases in SWNT yields are anticipated when a dual catalyst mixture is employed.

Understanding the Metal/Carbon Interaction Required to Observe Hydrogen Adsorption at Near Ambient Conditions. Hydrogen adsorption is observed at near ambient temperatures on the as-synthesized HWCVD MWNTs containing iron nanoparticles. No hydrogen adsorption, however, is

observed at near ambient temperatures for the purified MWNTs containing <0.5 wt.% iron. Figure 3 (top) shows temperature programmed desorption (TPD) curves of crude and purified MWNT materials following a room temperature H₂ exposure at 500 Torr with subsequent cooling to ~190 K and evacuation to $\sim 5 \times 10^{-8}$ Torr. Iron nano-particles purchased from Alpha Aesar were then incorporated in purified MWNTs as well as in μm -sized particles of graphite via sonication.

Figure 3 (bottom) shows TPD curves of these sonicated materials following the same hydrogen dosing procedure. No hydrogen adsorption was observed at near ambient temperatures when iron nano-particles were incorporated via sonication.

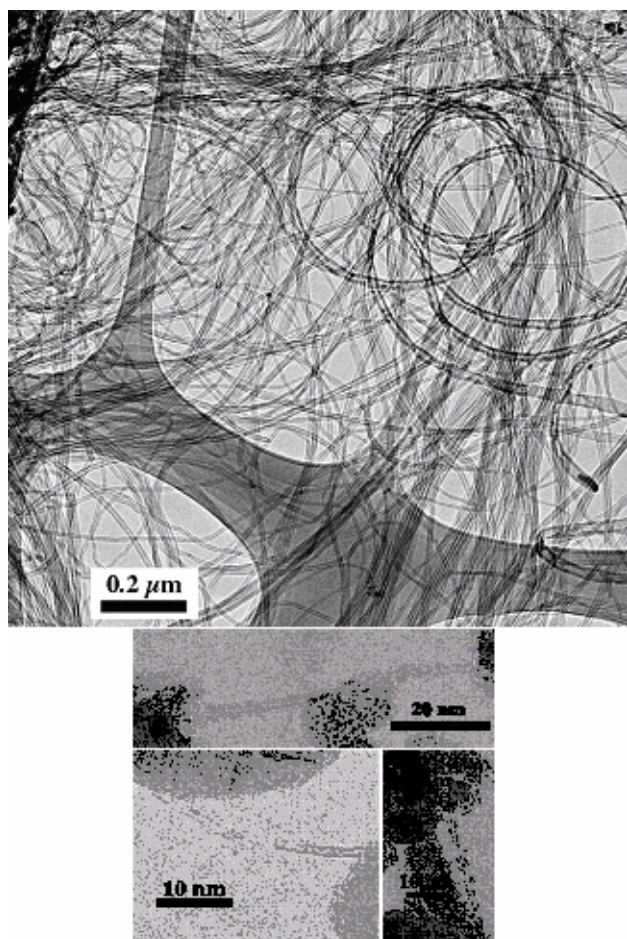


Figure 2. TEM Images of Crude HWCVD-Generated MWNTs (top) and Isolated SWNTs (bottom)

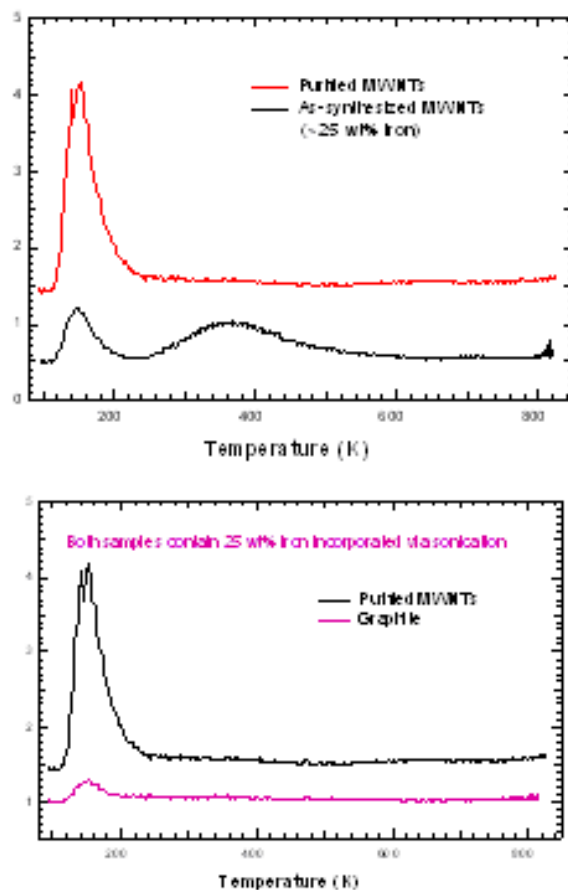


Figure 3. TPD H₂ Desorption Signals of As-Synthesized and Purified HWCVD-Generated MWNTs (top) and Purified MWNTs and Graphite with Iron Nano-Particles Incorporated via Sonication (bottom)

Figure 4 shows high resolution transmission electron microscope (TEM) images of the as-synthesized MWNTs (top) and the purified MWNTs following metal incorporation via sonication (bottom).

Note that in the as-synthesized materials, the iron nano-particle is located at the MWNT tip, while in the sonicated materials, the iron nano-particle randomly overlaps several nanotubes. These results, for the first time, conclusively demonstrate that small metal nano-particles must be in highly intimate contact with carbon nanotubes in order to observe hydrogen adsorption at near ambient conditions⁸.

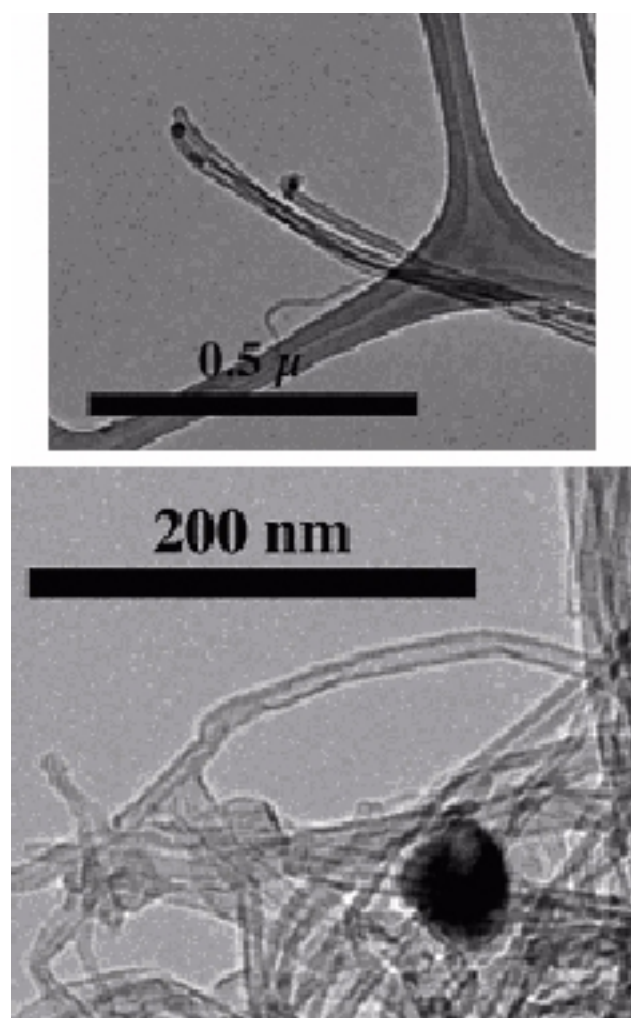


Figure 4. TEM Images of As-Synthesized HWCVD MWNTs (top) and Purified MWNTs with Iron Nano-Particles Incorporated via Sonication (bottom)

Controlled Incorporation of Ti into Purified, Cut SWNTs. Single-wall carbon nanotubes were produced via laser vaporization and subsequently cut by an oxidative process that does not introduce a metal hydride. The transport of Ti via TiI_4 is well known ($\text{Ti} + 2\text{I}_2 \rightleftharpoons \text{TiI}_4$). TiI_4 evaporates at 377°C (1 atm) and decomposes at higher temperatures. TiI_4 was vapor transported to purified, cut SWNTs at a higher temperature in the presence of H_2 in an effort to incorporate small particles of TiH_2 . Unfortunately, the formation of TiC is thermodynamically favored over the formation of elemental Ti or C at all temperatures. Even in the presence of H_2 , the titanium carbide was always formed, as shown by x-ray diffraction (XRD) measurements. No unusual hydrogen adsorption properties were observed for the SWNT samples containing titanium carbide.

Evaporation of thin films of Ti was also employed to establish a controlled method of metal incorporation in purified, cut SWNTs. Again, however, enhanced hydrogen adsorption was not observed for these samples. This behavior was attributed to the rapid oxidation of the Ti films. In the future, Pd evaporation will be explored since Pd is not susceptible to air oxidation at ambient conditions. Iron evaporation may also be employed since oxidation of the iron nano-particles is not detected with XRD in the as-synthesized MWNTs, even after several weeks of exposure to air.

Hydrogen Adsorption on Conducting Polymer and Non-Nanotube Nanocarbons. The hydrogen adsorption properties of several conducting polymers supplied by Prof. Alan MacDiarmid were explored. Figure 5 (top) shows the TPD spectrum of a PANI-CSA polymer treated with Triton-x that was degassed to 100°C and exposed to hydrogen at 760 Torr. For comparison, a TDP spectrum of a SWNT sample that was degassed to 1000°C and exposed to hydrogen at 500 Torr is also shown. In both cases, the sample was cooled to $\sim 190\text{ K}$ while the H_2 gas was evacuated. For the SWNTs, the low-temperature “peak” is most likely the tail of a larger peak that would dominate if the sample could be cooled to a lower temperature while still in the presence of 500 Torr H_2 . However, for the polymer sample, a peak with two shoulders is clearly observed above the

minimum temperature to which the sample is cooled. These results indicate that unique, higher-temperature hydrogen adsorption sites exist on this conducting polymer sample. Adsorption experiments conducted with a hydrogen overpressure could shift the H_2 desorption temperatures for the polymer to higher temperature, and these will be explored.

The hydrogen storage properties of nano-carbon samples produced by the decomposition of ferrocene in the HWCVD chamber were also examined. The sample was shown with TGA to contain 42 wt.% iron. An H_2 TPD curve for this sample following degassing in vacuum to 550°C and exposure to 500 Torr H_2 is shown in Figure 5 (bottom). For comparison, a TPD spectrum of as-synthesized HWCVD generated MWNTs containing 25 wt.% iron is also shown following the same dosing procedure. The nano-carbon sample actually displays a hydrogen adsorption capacity at near ambient conditions that is $\sim 10\times$ greater than that of the MWNT sample. Iron is not anticipated to store hydrogen at near room temperature. Further, the results of Figure 3 (bottom) clearly show that iron nanoparticles do not uptake hydrogen under the dosing conditions employed here. These results, therefore, conclusively show that non-nanotube carbons may also be promising candidates for vehicular hydrogen storage applications.

Conclusions

- Graphite-encapsulated metals are more easily removed from crude SWNT materials if CO_2 oxidation is employed prior to the conventional purification process.
- HWCVD has been developed as a continuous and scaleable technique for the production of MWNTs at high density. HWCVD has also been demonstrated for continuous production of SWNTs.
- Metal assisted hydrogen adsorption at near ambient conditions on carbon nanotubes only occurs when small metal nano-particles are in intimate contact with the tubes.
- The evaporation of Pd instead of Ti onto carbon nanotube materials will likely be more effective in hydrogen adsorption

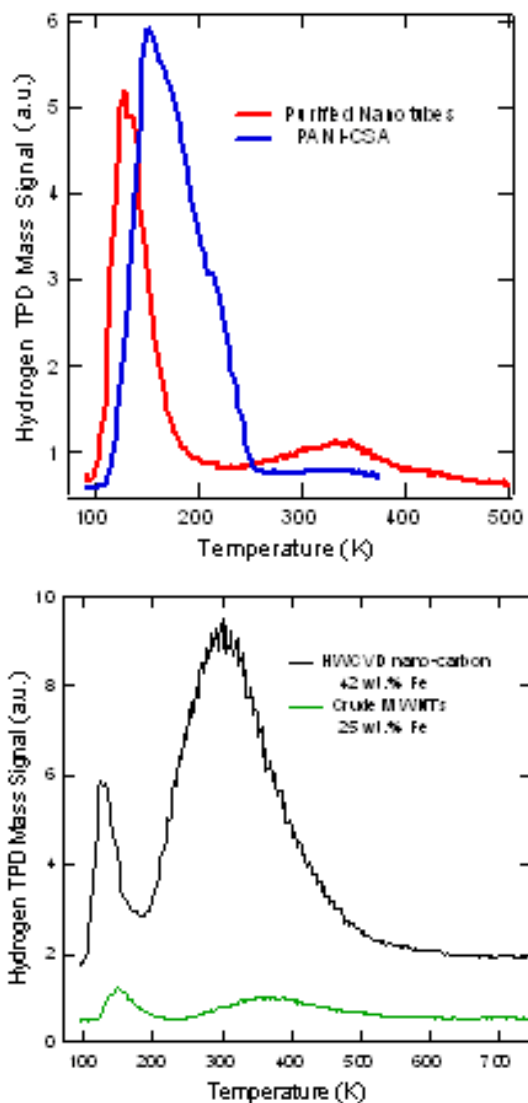


Figure 5. Hydrogen TPD Spectra of a Conductive Carbon Polymer Compared to Purified SWNTs (top) and HWCVD-Generated Nano-Carbon and Nano-Iron Particles Compared to HWCVD MWNTs (bottom)

catalysis since Pd is not oxidized in air at room temperature.

- Both conducting carbon polymers and HWCVD-generated Fe-doped nano-carbons are promising candidates for vehicular hydrogen storage materials.

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FY 2003 Publications/Presentations

1. Heben, M.J.; Dillon, A.C.; Gilbert, K.E.H.; Parilla, P.A.; Gennett, T.; Alleman, J.L.; Hornyak, G.L.; Jones, K.M. "Assessing the Hydrogen Adsorption Capacity of Single-wall Carbon Nanotube / Metal Composites" in *Hydrogen in Materials and Vacuum Systems*; American Institute of Physics, 2003; Vol. CP671, 77.
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Special Recognitions & Awards/Patents Issued

1. Patent continuation-in-part application: PCT/01-19 CIP "Hot Wire Production of Multi-Wall and Single-Wall Nanotubes." Dillon, A.C., Mahan, A.H. and Alleman J.L., March, 2003.
2. "Hot Wire Chemical Vapor Deposition of Isolated Carbon Single-walled Nanotubes", published in *Appl. Phys. Lett.* 81 (2002) 4061, was selected for the November 25, 2002, issue of the Virtual Journal of Nanoscale Science & Technology. The Virtual Journal is an edited compilation of links to articles from participating publishers, covering a focused area of frontier research.